Characterizing Disinfection By-product Formation Potential with UV Absorbance Techniques

Project Scope

Disinfection of drinking water with chlorine may produce undesirable, potentially toxic chemical byproducts. These disinfection by-products (DBPs) are organic and inorganic compounds formed by reactions between chemical oxidants, including chlorine and bromide, and dissolved organic matter (DOM) in the source water. EPA's recent multi-staged Disinfectant and Disinfection Byproducts Rule sets standards for the allowable levels of DBPs in drinking water, posing a challenge for public water utilities. Understanding the characteristics of natural waters that contribute to the formation of DBPs is necessary to develop cost-effective strategies to comply with the new standards.

The primary goal of this research was to study the relationship between the composition of the DOM and the formation of DBPs, specifically trihalomethanes (THMs) and haloacetic acids (HAAs). DOM composition varies widely (e.g., proteins and hydrocarbons from decayed plant matter) in source waters. Because different components react differently with disinfectants, knowledge of DOM composition and how it relates to reactivity is central to improved control of DBPs.

The researchers investigated the use of a spectroscopic measure, specific ultraviolet absorbance (SUVA), to predict DOM reactions with disinfectants. The SUVA analytical method approved in the DBP rule (absorbance at 254 nm) is nonspecific and provides little direct information concerning the chemical composition or characteristics of DOM. Although SUVA can identify a high potential for DBP formation, SUVA alone does not provide specific information useful for deciding how to limit their production. This research improves the predictive power of SUVA measures by developing and testing a new "reactivity profile" methodology that expanded the utility of SUVA for guiding water treatment decisions.

Grant Title and Principal Investigators

Brominated DBP Formation and Speciation Based on the Specific UV Absorbance Distribution of Natural Waters (EPA Grant #R828045)

James E. Kilduff, Rensselaer Polytechnic Institute; Tanju Karanfil, Clemson University

Key Findings and Implications

Analytical Accomplishments:

- Reverse osmosis can effectively and rapidly isolate large quantities of dissolved organic matter (DOM) from natural waters without altering its physicochemical properties. This allows researchers to better characterize DOM and its role in disinfection by-product (DBP) formation.
- DOM isolation and/or fractionation procedures using adsorption and ultrafiltration did not alter either the specific ultraviolet absorbance (SUVA) or the reactivity of DOM (in terms of DBP formation and speciation) as compared to the source water.
- Unique reactivity profiles that predict DBP formation as a function of SUVA were obtained from four different source waters. The source water profiles did not depend on the fractionation methods used to obtain them.
- Although SUVA and chlorinated DBP formation were positively correlated, bromide was found to be preferentially incorporated into low-SUVA components of DOM.
- Anion exchange effectively removes DOM from solution and reduces DBP formation during chlorination.

Implications of Research:

- SUVA-based reactivity profiles may be useful for water utilities in predicting and managing DBP formation.

Publications include 8 peer reviewed articles and 7 conference presentations.

Project Period: March 2000 to March 2003

Relevance to ORD's *Drinking Water Research Multi-Year Plan* (2003 Edition)

This project contributes directly to the third of three Long-term Goals for drinking water research: (3) by 2010, develop scientifically sound data and approaches to assess and manage risks to human health posed by exposure to regulated waterborne pathogens and chemicals, including those addressed by the Arsenic, M/DPB, and Six-Year Review Rules.

Specific ultraviolet absorbance (SUVA) is known to be a reliable predictor of dissolved organic matter (DOM) and disinfection by-product (DBP) formation potential. This research project found that more fine tuned predictions of DBP formation that are tailored to specific source waters can be achieved by SUVA evaluation of fractionated DOM. The research also indicates that anion exchange can be an effective, low-cost method for DOM removal and subsequent reduction in DBP formation. Knowledge gained from this research should increase the ability of drinking water utilities to optimize treatment protocols to comply with the national Disinfectants and Disinfection Byproducts Rules.

Project Results and Implications

Reverse Osmosis for DOM Isolation: The researchers first tested a method to isolate large quantities DOM from natural waters for subsequent analysis without altering its physicochemical properties. In a series of tests, they evaluated the effectiveness of using reverse osmosis, a pressure-driven membrane process, to remove organic carbon from large volume source water samples. Sources sampled included the Tomhannock Reservoir in New York, and the Intercoastal Waterway, Edisto River, and Lake Bowen in South Carolina. The investigators tested and compared physicochemical properties of DOM isolated with reverse osmosis to DOM isolated using the traditional method—filtration with a 0.45-µm filter. The researchers measured the $SUVA_{254}$ and DBP formation and speciation. In addition, DOM isolated by reverse osmosis and 0.45-µm filtered source water exhibited similar physical and chemical properties in a number of other assays. These results provide strong evidence that reverse osmosis isolation preserved the integrity of DOM from the low-hardness surface waters that were tested.

XAD-8 Resin Adsorption and Ultrafiltration Fractionation of DOM: XAD-8 resin absorption and ultrafiltration can both be used to separate components of DOM; the former technique exploits differences in hydrophobicity, while the latter separates components by molecular weight. The effects of these two methods on DBP formation were compared. Investigators found that although there was no apparent relationship between molecular weight of the fractions obtained by ultrafiltration and DBP formation, there were significant differences associated with the varying aromatic content (the proportion of compounds with benzene rings) of the fractions obtained by XAD-8 absorption. These results support the concept that SUVA is a "distributed parameter" arising from a range of DOM components that can be used to predict DBP formation from a range of natural waters.

DBP Reactivity Profiles of Source Waters: The DBP formation potential of samples from four sources (Edisto River, the Intercoastal Waterway, Tomhannock River, and a stream draining a rural agricultural watershed in Rensselaer County, New York) was compared in this study. Consistent with previous reports, the investigators found that that granular activated carbon, XAD-8 adsorption, and alum coagulation preferentially removed high-SUVA components from water, and that UV-absorbing compounds were associated with for DBP formation. However, although SUVA appears to be an accurate predictor of reactivity with chlorine in terms of DBP yield, it was found that low-SUVA components were more reactive to bromine incorporation. For a given source water, a consistent correlation was observed between the SUVA values of specific DOM fractions and the amounts of THMs and HAAs produced, independent of the separation process used to obtain the fractions. Therefore, the investigators concluded that the results reflect the natural DBP reactivity profile of DOM from each source water. A unique reactivity profile, reflecting the formation of specific DBPs as a function of SUVA, was obtained for each water tested. This suggests that source water-specific reactivity profiles

can be used to predict the amounts and species of DPBs likely to be formed during disinfection. The researchers suggested that periodic SUVA profiling may be useful for on-line monitoring and control of DBP formation by water utilities.

Ion Exchange for Removal of DOM from Source Waters: The effectiveness of anion exchange in removing DOM from sources water, and in reducing DBP formation, was evaluated in this study. Researchers found that anion exchange reduces dissolved organic carbon levels by as much as 70 percent, and reduces DBP formation between 50 and 90 percent, depending on the source waters. The SUVA-reactivity profiles for DBP formation were again found to be different and distinctive for different source waters.

Investigators

J.E. Kilduff, Rensselaer Polytechnic Institute
T. Karanfil, Clemson University

For More Information

NCER Project Abstract and Reports:

http://cfpub2.epa.gov/ncer_abstracts/index.cfm/fuseaction/display.abstractDetail/abstract/820/report/0

Peer Reviewed Publications

Kitis, M., Kilduff, J.E., and Karanfil, T. 2001. Isolation of dissolved organic matter (DOM) from surface waters using reverse osmosis and its impact on the reactivity of DOM to formation and speciation of disinfection by-products. Water Research 35(9):2225-2234.

Kitis, M., Karanfil, T., Kilduff, J.E., and Wigton, A. 2001. The reactivity of natural organic matter to disinfection by-products formation and its relation to specific ultraviolet absorbance. Water Science and Technology 43(2):9-17.

Kitis, M., Karanfil, T., Wigton, A., and Kilduff, J.E. 2002. Probing reactivity of dissolved organic matter for disinfection by-product formation using XAD-8 resin adsorption and ultrafiltration fractionation. Water Research 36(15):3834-3848.

Kilduff, J.E., Mattaraj, S., Wigton, A., Kitis, M., and Karanfil, T. 2004. Effects of reverse osmosis isolation on reactivity of naturally occurring dissolved organic matter in physicochemical processes. Water Research 38(4):1026-1036.

Kitis, M., Karanfil, T., and Kilduff, J.E. 2004. The reactivity of dissolved organic matter for disinfection by-product formation. Turkish Journal of Engineering and Environmental Sciences 28(3):167-179.

Tan, Y., Kilduff, J.E., and Karanfil, T. 2004. Ion exchange for controlling disinfection-byproduct formation via precursor removal. Desalination 176:189-200.

Baxley, J.M., Hepplewhite, C., and Karanfil, T. 2004. The efficiency of the ILUV oxidation method for organic nitrogen analysis. Water Science and Technology: Water Supply 4(4):25-32.